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(54) **A floor or wall covering**

(57) A floor or wall covering material resistant to the migration of organic products such as plasticizers, comprises a continuous barrier layer made up of a material which is impervious to plasticizers e.g. a film of polyethylene terephthalate, polytetra-fluorethylene or an acrylic resin modified polyester polyurethane. The barrier layer may be interposed between the backing and decorative wear layers of the covering; alternatively it may form the backing layer. In making the covering the wear layer may be applied to the barrier layer by coating the barrier layer with polyvinyl chloride, applying the decoration by printing and overlying the decoration with a transparent coating of polyvinyl chloride.

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FIG. 1

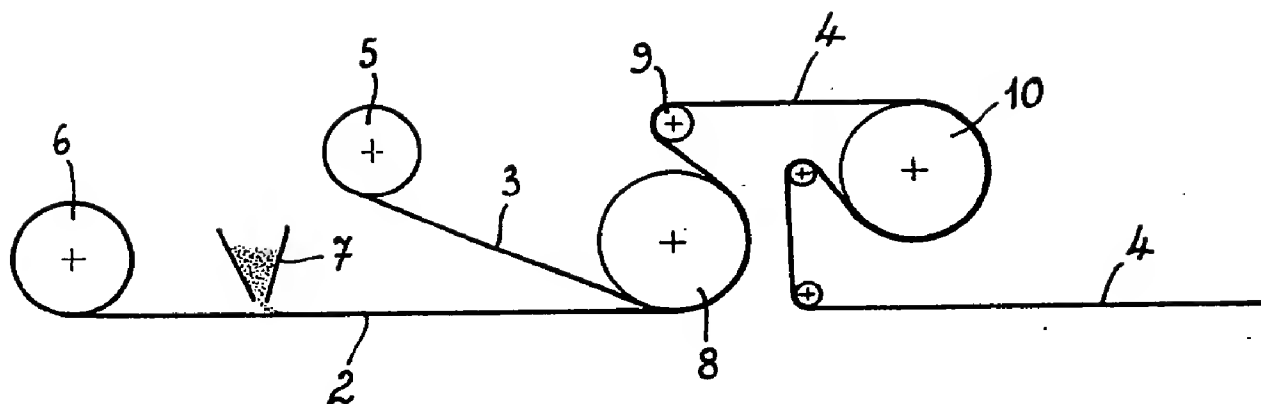


FIG. 2

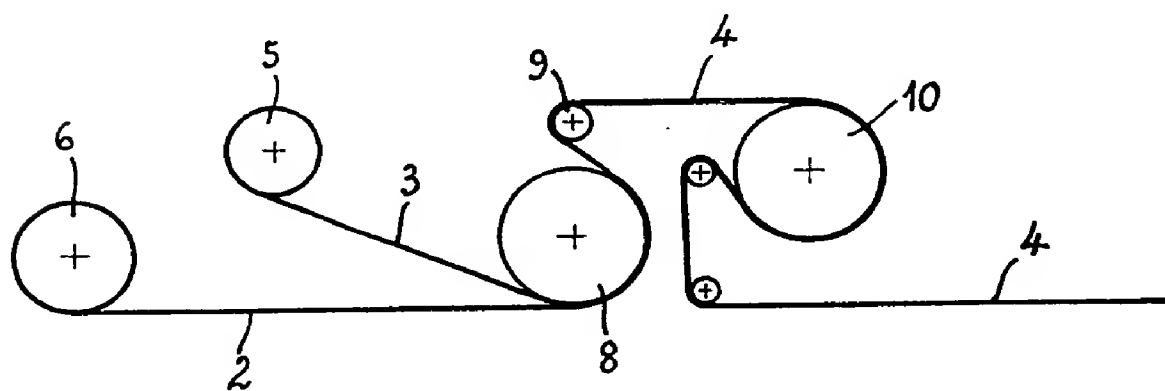
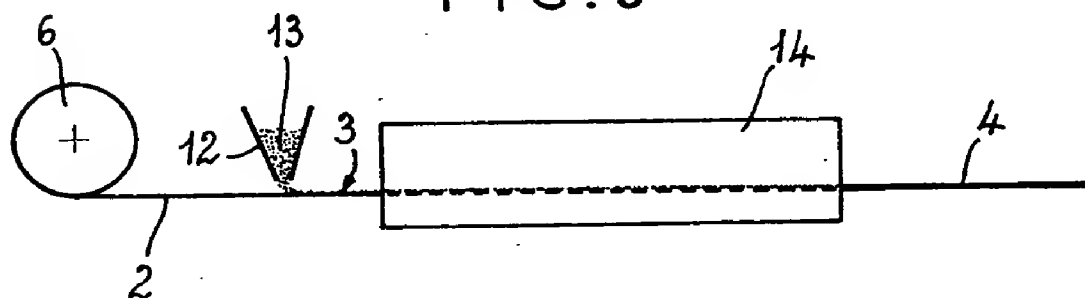


FIG. 3



SPECIFICATION

A floor or wall covering

5 The present invention concerns a floor or wall covering, proof against the migration of organic products and particularly plasticizers, and also a process of manufacture of such a covering. 5

It is known that the migration of certain elements through the various component layers of vinyl floor or wall coverings, and in particular coverings which have a transparent rear surface poses important problems when these coverings are put into use, especially with regard to the alteration of their external appearance.

10 Examples of such phenomena are the migration of steam, resulting in the appearance of white, opalescent stains, the migration of plasticizer products leading to soiling particularly in places where wear is greatest, and/or the migration of other organic products or coloured minerals, either alone or carried by the above mentioned plasticizers, forming coloured stains which are all the more visible in a thicker transparent layer. 10

The study of these phenomena has lead the Applicant to investigate means of achieving a covering which is proof against such migrations and especially against the migration of plasticizers, this covering necessarily including at least one continuous barrier layer. 15

There are already in existence composite coverings which incorporate an additional layer. French Patent Application No. 2 295 838 describes a covering reinforced with fibres and made up of a layer of foam with a supplementary underlying layer. But the principal aim of this additional layer is to improve the elasticity and the acoustic properties (soundproofing) of the composite covering obtained. The very nature of this layer (a vinyl chloride polymer which may itself be plasticized) even though it might permit it to act as an obstacle to the migration of the glue, it makes it ineffective against the products of the metabolism of cryptogenic organisms, since cryptograms feed on the plasticizers contained in the layer of their coloured metabolic by-products migrate into the plasticizers and appear in the form of stains in the transparent layer which is exposed to wear. In the same way, the composition of the additional layer described in the French Patent Application No. 2 295 838 prevents it from forming an obstacle to the migration of plasticizers which may be present in the products used in subsequent treatment steps. The sensitivity of plastisols to plasticizers is in fact well known. 20 25

We have thus investigated the means of achieving a vinyl covering which is proof against the migration of organic products and especially plasticizers. The aim of the Applicant is to achieve a covering which includes a continuous layer, forming a barrier, and comprising a material which is chemically inert towards organic products, the migration of which is to be prevented, and especially plasticizers. 30

According to this invention we provide a floor or wall covering material resistant to the migration of organic products such as plasticizers, characterised in that it comprises a continuous barrier layer made up of a material which is impervious to plasticizers. 35

According to one particular form of embodiment, the continuous barrier layer is interposed between the back layer of the covering and the decorated wear layer.

The continuous barrier layer may alternatively itself form the back layer of the covering.

The continuous barrier layer is preferably made up of a film of polyester and more especially a film of polyethylene glycol terephthalate. It can equally well be made of a film of polytetrafluorethylene. 40 Alternatively, the continuous barrier layer may comprise a polymer of a polyurethane-polyester copolymer modified by an acrylic resin.

It is, moreover, often necessary, from an aesthetic viewpoint, to mask from the eyes of the user, any stains which form under the barrier layer and which, without migrating through the latter, can show up by virtue of its transparency and detract from the good looks of the exterior of the covering. 45

Thus, where the barrier layer is transparent, an opaque layer may be interposed between the barrier layer and the transparent wear layer.

According to another form of embodiment, the film constituting the barrier layer can itself be coloured, thus rendering unnecessary the presence of the opaque layer.

50 The invention also concerns a method of manufacture of the covering material according to the invention. According to one embodiment, the film constituting the barrier layer is applied by adhesion with the application of heat to the back layer covered in plasticized P.V.C. and the heat treatment at the same time assures the pre-gelling of the layer of P.V.C.

The film constituting the barrier layer can also be applied by adhesion with the application of heat to the back layer covered with pre-gelled plasticized P.C.V. 55

According to another form of embodiment, the film constituting the barrier layer may be obtained by a known process (e.g. coating thousand pointed roller), of a cross-linkable, film forming product in the form of a true solution or emulsion, followed by a crosslinking treatment brought about in known manner, by thermal treatment, or by ultra-violet radiation or an electron beam.

60 The present invention will moreover be better understood with the aid of the following description and with reference to the adjoining diagram in which:

Figures 1 and 2 are diagrammatic view of a production line for the barrier layer part of the covering in which the barrier layer is obtained by glueing on a continuous film.

Figure 3 is a diagrammatic view of a production line for the barrier layer part of the covering in which the barrier layer is obtained by the application of a true solution or an emulsion of a cross linkable film forming 65

product.

In Figures 1, 2, and 3 the covering material comprises a base 2 making up the back layer of the covering, a barrier layer 3 and a part which is proof against migration 4.

As can be seen in Figure 1, a continuous film of material resistant to plasticizers and making up the barrier layer 3, unwinding from the roller 5, is applied by a continuous process, to the surface, previously covered in plasticized polyvinylchloride, by means of the device diagrammatically shown at 7, of the back layer 2 unwinding from the roller 6. The operation of adhering together the film constituting the barrier layer 3 and the back layer 2 constituting the base of the covering is brought about by passing them over the cylinder 8, heated to a temperature depending on the nature of the film to be adhered, between 60°C to 180°C, and preferably between 125 and 140°C. This heat treatment simultaneously ensures the pre-gelling of the layer of previously-plasticized P.V.C. applied to the base of the covering.

In the device shown in Figure 2, the continuous film constituting the barrier layer 3 unwinding from the roller 5 is applied, according to a continuous process, to the surface of the back layer 2 which has been previously coated with plasticized and pre-gelled P.V.C., this layer unrolling from the roller 6. The operation of adhering together the film constituting the barrier layer 3 and the back layer 2 constituting the base of the covering is brought about by passage over the cylinder 8, heated to a temperature which depends on the nature of the film to be adhered, from 60 to 180°C, and is preferably from 125 to 140°C.

After passing over the small direction-changing rollers 9, the migration-proof compound which is obtained is cooled, in known manner by passing it over a cooling cylinder 10.

The film constituting the barrier layer 3 can be made up of any continuous film which is resistant to plasticizers. It may thus be a film of polytetrafluoroethylene or a film of polyethyleneglycol terephthalate. In these cases, pre-treatment of the film is necessary to make it adhere to the P.V.C., this pre-treatment possibly being carried out on the production line itself by a known device (e.g. coating or heliographic cylinder) which is not shown. One can equally well use a polyester film already pre-treated at the time of its manufacture.

In the embodiment shown in Figure 3, the migration proof barrier 3 is obtained by the application, with the aid of a device diagrammatically shown at 12, of a true solution or an emulsion of a film forming, cross-linking product 13 to the surface of the back layer 2 which has been previously coated with plasticized P.V.C., unwinding from the roller 6 by known device, such as a coating, thousand point roller, or heliographic cylinder device, suitably for applying a uniform quantity of the film forming cross-linking product 13 over the whole surface of the back layer 2.

The back layer 2 covered in the film-forming cross-linking product 13 then passes into the cross-linking device 14 which can be a hot air cabinet, an Ultraviolet radiation chamber or electron beam device, according to the nature of the product to be cross-linked. It is in this device 14 that the formation of the barrier layer 3 will be completed in the form of a continuous film, proof against migrations, by the evaporation of the solvent or by the breakdown of the emulsion, and by the cross linking of the film-forming product. The compound 4 emerging from the device 14 therefore, as in the previous embodiment, comprises a base of the covering 2 and the barrier layer 3.

The film-forming product 13 can be made up of any solution or emulsion which, after cross-linking is capable of forming a film which is resistant to plasticizers.

This may be a polymer or a copolymer polyurethane-polyester modified by an acrylic resin.

Depending on the nature of the film forming product applied, it may also be necessary after the cross linking operation, to carry out a process for adhering it to the P.V.C. (a process known in itself and not shown) for the purpose of ensuring that the compound achieved has good adhesion.

The conventional operations for forming a vinyl floor or wall covering follow and they are not shown in the drawing.

In the case of transparent barrier layer 3, the surface of the compound 4 which has the barrier layer 3 is covered with an opaque layer designed to conceal from the eyes of the user the possible stains produced under this barrier without however passing through it. It is of course understood that where the barrier layer 3 is itself opaque or coloured, the presence of this opaque layer is not necessary. The decoration is then applied by printing, either onto the barrier layer 3, or onto the opaque layer, and finally a transparent surface for exposure to wear is applied on top of the decoration.

The base of the covering or the back layer 2 can be of any material conventionally used for the purpose, e.g. a non-woven fabric or felt covered with a vinyl plastisol, a pressed vinyl sheet, an embossed, expanded vinyl covering, with or without polyester support.

The following examples further illustrate the invention without limiting it in any way.

Example 1

Onto a base 2 made up of a textile or mineral support covered in plasticized P.V.C. having the following composition:

60	P.V.C.	100	60
	Plasticizer	(phthalate)	125
	Extenders	(mineral oils)	5
	Fillers	(calcium carbonate)	400
65	Stabiliser	(zinc octoate)	2
			65

a film 3 of transparent polyethyleneglycol terephthalate, pretreated for adhesion to P.V.C. of the type "Melinex", Registered Trade Mark (ref. 542 -I. C. I.) of a thickness of 36 μ is applied according to the process described with reference to Figure 1. The combination of base 2 and film 3 passes over a cylinder 8 at 120°C, where both the pre-gelling of the P.V.C. and the adhering together are brought about, then on to a cooling cylinder 10, resulting in the production of the laminar material 4. The speed of production is 10 metres/minutes.

The surface of the laminate 4 bearing the film 3 is coated with a layer of plasticized, opaque P.V.C. having the following composition:

10	P.V.C.		100	10
	Plasticizer	(Phthalate)	60	
	Stabilisers	(Ba, Ca, Zn)	2	
	Titanium Oxide		10	
	Filler	(calcium carbonate)	60	

15 The decoration is then applied to the surface of the opaque layer by heliographic printing in the classic manner, then on top of the decoration a transparent layer for exposure to wear is applied having the following composition:

20	P.V.C.		100	20
	Plasticizer	(Phthalate)	30	
	Exoxidised oils		3	
	Stabilisers	(Ba, Ca)	2	

25 In this way there is obtained a covering which is perfectly proof against the migration of plasticizers, the base layer of which accumulates in the course of wear, the cryptogamic organisms and their by-products, which give it a perpetually red colouring masked by the opaque, white layer which visually isolates the decoration from the base layer.

30 *Example 2*
On a covering base 2 made up of a pre-gelled, plasticized P.V.C. base with the following composition:

	P.V.C.		100	
	Plasticizer	(phthalate)	125	
35	Diluents	(mineral oils)	5	35
	Fillers	(calcium carbonate)	400	
	Stabiliser	(zinc octoate)	2	

40 a film 3 of transparent polyethylene glycol terephthalate of the same type as described in Example 1 is applied according to the process described with reference to Figure 2. The combination of base 2 and film 3 passes over a cylinder 8 at 120°C where the adhering together is brought about, and then on to the cooling cylinder 10, leading to the formation of the laminate 4. The speed of production is 100 metres/minute.

The order of operation is the same as described in Example 1.

45 *Example 3*
There is directly applied to a film 3 of transparent polyethylene glycol terephthalate, of the type described in 1, a layer of plasticized opaque P.V.C. having the following composition:

	P.V.C.		100	
50	Plasticizer	(phthalate)	60	50
	Stabilisers	(Ba, Ca, Zn)	2	
	Titanium oxide		10	
	Filler	(calcium carbonate)	60	

55 The order of operations (application of decoration and transparent layers for exposure to wear) is the same as described in Example 1.

In this case, it is the barrier layer which constitutes the back layer of the covering which is impervious to migrations according to the invention.

60 *Example 4*

On a base of covering 2 similar to that described in Example 2, there is applied, by means of a thousand point woven cylinder, 15g/m² of a solution of a polyurethane modified by an acrylate of the type sold commercially under the trademark "Quinn L G 3647 C" by the Quinn Company, the viscosity of which may be regulated with the aid of monomeric acrylic viscosity-reducing agent.

65 The obtaining of the laminate 4 made up of the base 2 and the barrier layer 3 of modified polyurethane film

is ensured by the passage through an ultra-violet drying tube at a speed of 11 metres/minute there is then carried out on the cross-linked barrier layer an adhesion treatment to allow the adhesion to further layers of P.V.C. This treatment is brought about by the application of 3g/m², with a thousand point roller, of a 10% solution in methylcelcetone of a polyester resin "ADCOTE 1077" (sold by the Company NORTON AND WILLIAMS), followed by a reactivation treatment at 120°C.

The application of the opaque layer, the decoration and the wear layer take place under the conditions described in Example 1.

CLAIMS

- 10 1. A floor or wall covering material resistant to the migration of organic products such as plasticizers, characterised in that it comprises a continuous barrier layer made up of a material which is impervious to plasticizers. 10
- 15 2. A covering material according to claim 1; characterised in that the continuous barrier layer is interposed between a back layer of the covering, and a decorated surface layer which is to be exposed to wear. 15
3. A covering material according to claim 1, characterised in that the continuous barrier layer itself constitutes a back layer of the covering.
4. A covering material according to any of claims 1 to 3, characterised in that the continuous barrier layer 20 comprises a polyester film. 20
5. A covering material according to claim 4, wherein the polyester film is a film of polyethyleneglycol terephthalate.
6. A covering material according to any of claims 1 to 3, characterised in that the continuous barrier layer comprises a film of polytetrafluorethylene.
- 25 7. A covering according to either of claims 1 or 2, characterised in that the continuous barrier layer comprises a polyurethane-polyester copolymer modified by an acrylic resin. 25
8. A covering material according to any of claims 1 to 6, characterised in that an opaque layer is interposed between the barrier layer and the transparent wear layer.
9. A covering material according to any of claims 1 to 6, characterised in that the barrier layer is opaque.
- 30 10. A process for the manufacture of a floor or wall covering material according to any of claims 1, 2, 4, 5 or 8 characterised in that a film to constitute the barrier layer is adhered with the application of heat to the back layer which is covered with plasticized P.V.C. so that the heat causes simultaneous pre-gelling of the P.V.C. 30
11. A process according to any of claims 1, 2, 4, 5, 7 or 8 characterised in that the film making up the barrier layer is adhered with the application of heat to the back layer which is covered with pre-gelled plasticized P.V.C. 35
12. A process for the manufacture of a covering material according to any of claims 1, 6, 7 or 8 characterised in that the film making up the barrier layer is obtained by the application of a film-forming cross-linking product in the form of a solution or emulsion, followed by a cross-linking treatment.